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Biaxial Effects in Nematic Comblike Polymers

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ABSTRACT: Comb polymers consisting of semiflexible main chains and rodlike side chains form complex nematic phases, largely as the result of competition between polymer entropy and the nematic order of the component parts of the molecule. The competitive effects are modeled by choosing different molecular architectures and thus different strengths of molecular inteactions. The molecular interactions are chosen to have the simplest possible form and are modeled using a mean field theory. The five nematic phases found are called N_I, N_{II}, N_{III}, N_{IB}, and N_{IIB}. The N_I, N_{II}, and N_{III} phases are uniaxial and have at least one component, main or side chain, ordered in a particular direction. The biaxial phases N_{IB} and N_{IIB} have each component ordered in directions perpendicular to each other. This has unusual consequences, resulting in the symmetry of the component order parameters being lower than that of the component interactions. Consequently the main-chain conformation becomes anisotropic in three directions. These biaxial phases represent intermediate states as architecture is varied between the uniaxial states N_I and N_{II}.

1. Introduction

Polymer liquid crystals (PLCs) exhibit many unusual phenomena as a consequence of competition between orientational ordering, due to their liquid crystal character and the drive toward maximum entropy common to all chain systems. Comb polymer systems provide further opportunities for richness of behavior,[1-3] with unusually ordered liquid crystalline states being observed. Comb molecules are modeled in this paper by taking a wormlike polymeric main (backbone) chain with its own intrinsic flexibility and nematicity and attaching rigid rodlike nematic side chains to the backbone with hinges which can be of varying stiffness. This is the approach of ref 2. The new nematic phases arise because the nematic influences of the component parts of the polymer are in competition. The stiffness of the hinges governs many of the properties of the comb molecule, for unless the hinges are very weak, the side chains force the main chain to order in a direction different from that of the side chains. As only orientational and not spatial interactions are considered only nematic, not smectic, phases will be discussed.

The emphasis of the paper is concentrated on modeling the molecular interactions as simply as possible. All nematogens are assumed to be cylindrically symmetric rods, which interact via mean fields. With even these simple interactions the phase behavior of the system is very complex. A more realistic approach would result in behavior qualitatively of the form yielded by the minimal model. Rather than try to model a particular system by estimating the molecular interaction parameters, typical values of the parameters are chosen to illustrate as fully as possible the richness of phase behavior possible. Even with main and side chains geometrically uniaxial (cylindrical), biaxial phases emerge because of the geometry of their attachment. This type of biaxiality is quite different from the biaxiality first discussed theoretically[4] and observed later observed experimentally[5,6] in low molecular weight liquid crystals. That biaxially arises because the molecules are long and flat, rather than the cylindrical shape which characterises uniaxial nematics. That the geometry of attachment of cylindrical objects can lead to biaxiality was first envisaged by Rusakov and Shliomis[3] for rigid combs. They considered teeth rigidly radiating out from a rigid backbone, the backbones not suffering mutual interactions or interacting nematically with the teeth. They also made passing reference to the worm case.

In previous work[2] using a similar theory, on which this work draws heavily, three nematic phases were found, denoted by N_I, N_{II}, N_{III}. However that theory and the earlier lattice approach[1] was not sufficiently general to allow both components, the side chains and the backbone, to order simultaneously in different directions. The possibility that biaxial phases could exist in comb molecules as intermediates between these uniaxial phases had been suggested by earlier authors.[2,3,7] The predictions of the new more general theory are that phases denoted by N_{IB} and N_{IIB}, which have simultaneous ordering in more than one direction, form in preference to N_I and N_{II} under some conditions. In these new phases the molecule as a whole becomes biaxial, the main chain and side chains each having a separate major axis of symmetry. The order parameters of each component also display a small amount of biaxiality with the consequence that the backbone chain conformation becomes anisotropic in three directions. This is unusual because the macroscopic symmetry of each component is lower than the symmetry of the molecular interactions, a result of coupling the two phases together.

Figure 1 sketches the five possible nematic phases. In N_I the hinge units are stiff and the side chains dominate the ordering. This forces the backbone into the xy plane. N_{II} occurs when the main-chain ordering influence is very strong, and the hinges are again stiff. The main-chain ordering then forces the side chains into the perpendicular plane. If the hinges are overcome by the nematic forces of the side chains, the side chains could order in the same direction as the main chain, this phase is denoted by N_{III}. There can only be three stable uniaxial phases if we have two coupled order parameters (for side and main chains), and at least one of them must be positive. We are interested in new phases that are intermediate to N_I and N_{II}. When the molecular hinge is stiff and the temperature low enough, N_{IB} and N_{IIB} occur, either from a transition from N_I or N_{II}, respectively, or straight from the isotropic phase. In these phases both the backbone and the side chains are ordered, but in different directions. The new phases can be thought of as having envolved from N_I or N_{II}. For instance, in N_{II} rods are compelled to lie in the perpendicular plane. If eventually their own nematic influences become strong compared with the

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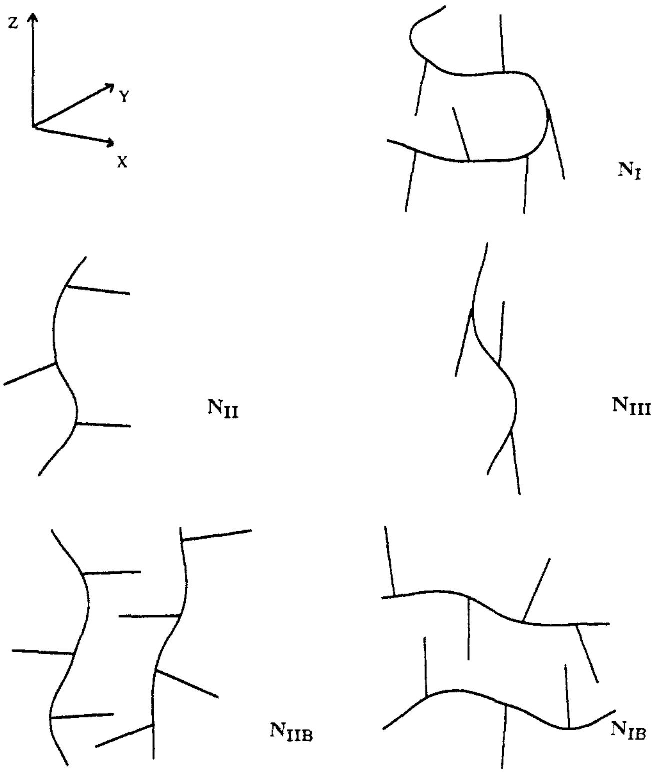

Figure 1. The five nematic phases possible for comb polymers. The phases N_I, N_{II}, and N_{III} are uniaxial with at least one component ordered in a definite direction. The phases N_{IB} and N_{IIB} are biaxial and have simultaneous ordering of the backbone and side chains in different directions. The N_{IB} and N_{IIB} diagrams are identical, but rotated through 90° to stress the fact that N_{IB} and N_{IIB} are physically identical even though they have quite different order parameters. All phases are drawn with very high degrees of order.

thermal energy k_BT, they choose a unique direction in the plane along which to order. This order is not uniaxial about this direction since the backbone influence acts principally from only one other axis; i.e., the system as a whole is biaxial. It is obvious that given the same molecular structure and temperature the N_{IB} and N_{IIB} phases are identical—they are just viewed from different coordinate systems where the principal axis is either that appropriate to the backbone or to the side chains. Thus an arbitrary distinction has to be made as to when it is appropriate to call a phase N_{IB} or N_{IIB}. This is discussed further in section 5. The phase transitions between the N_I and N_{II} phases and their respective biaxial counterparts can be either first or second order. An analogy of the phase transitions between pairs of states is made by modeling the side-chain system as a set of independent rods in a "negative" field, in an attempt to more fully understand the nature of the transitions. In section 2 we discuss order parameters and interactions, in section 3 the wormlike chain model, in section 4 a mean field theory of combs allowing biaxial phases, in section 5 the results of the theory including phase diagrams and molecular conformations, and in section 6 we conclude.

2. Order Parameters and Mean Fields

We are going to describe complex phases composed of molecularly uniaxial components. Biaxiality arises because the component molecules can have an orthogonal relative orientation imposed upon them. For this reason we now summarize the geometry of the order parameter tensor. The nematic phase of a liquid is characterized by the long-range orientational order of the constituent molecules. This results in the response functions of the bulk material, i.e., the diamagnetic susceptibility, dielectric permittivity, being anisotropic. The order parameter matrix, a traceless symmetric second-rank tensor, describes this anisoptropy. As the tensor is symmetric it is always possible to find a frame of reference in which it is diagonal. The conventional parameterization (see ref 8) is

$$Q_{\alpha\beta} = \begin{pmatrix} \left(-\frac{1}{2}Q + \frac{1}{2}X\right) & 0 & 0 \\ 0 & \left(-\frac{1}{2}Q - \frac{1}{2}X\right) & 0 \\ 0 & 0 & Q \end{pmatrix} \tag{1}$$

Q and X are themselves known as order parameters and are just numbers that characterize the physical system. Their relationship to the microscopic structure of the system is given below. The normal convention that the uniaxial phase exists and is ordered in the z direction is that $Q > 0$. Note that $+X$ and $-X$ are equivalent. This parameterization allows three different uniaxial phases as well as the possibility of a biaxial phase. The uniaxial phases are $Q_1 \neq 0$, $X_1 = 0$; $Q_2 \neq 0$, $X_2 = \pm 3Q_2$, which correspond to alignment along the z, x, y axes, respectively. When the previous relations are not obeyed, the phase is biaxial. The other choices of uniaxial axes are mentioned since the transition between the two uniaxial phases N_I and N_{II} via biaxial intermediates will involve changing the unique axis. If the unique axis is changed from z to x or y, X no longer directly measures the biaxiality of the phase. The biaxiality can be extracted by determining the largest element of the order parameter matrix, whereupon the biaxiality is the difference between the other two elements.

The macroscopic order of the system has to be somehow related to the microscopic properties of the constituent molecules. By use of a mean field theory, the interaction between individual molecules can be reduced to the interaction of one molecule with the average or mean field of all the others (as in the Curie–Weiss theory of paramagnetism). The value of this field then has to be self-consistently determined. It is a macroscopic characteristic of the system as whole, so the mean fields determined by using the microscopic parameters are themselves the macroscopic order parameters. First the interaction appropriate for a mean field theory of cylindrically symmetric rods is derived. This is then used to describe the interaction of mesogens incorporated into the main chain, and for the side chains themselves.

The simplest way of modeling the interaction between cylindrical rods is to use a pairwise $P_2(w)$-like potential[9] of quadrupolar symmetry appropriate to this molecular geometry. Here $w = \cos\vartheta$ and ϑ is the angle between the long axes of the molecules. $P_2(w)$ is the lowest order Legendre polynomial which is invariant under the rotation $\vartheta \rightarrow \pi - \vartheta$. The orientational interaction between molecules 1 and 2 can therefore be written as

$$U_{12} = -aP_2(w) \tag{2}$$

where a is the strength of the interaction. Although we shall obtain ordering in two directions, one coupling constant is sufficient to demonstrate this; see the geometry arguments of section 1. Since we are going to employ mean field theory, it is convenient to refer all molecular to one coordinate system, which is chosen to be the z axis, parallel to the symmetry axis of the uniaxial phase. Using Euler angles, the angle between the molecules 1 and 2 is $\Omega = (0, \vartheta, 0)$. This can be written as the sum of two Euler angles, Ω_1 and Ω_2, Ω_1 being the rotation from molecule 1 to the z axis, Ω_2 from the z axis to molecule 2 (see Figure

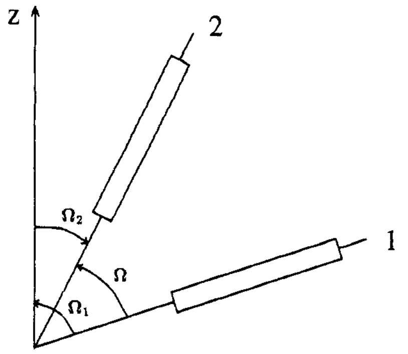

Figure 2. Decomposition of the Euler angle Ω between molecules 1 and 2 into Ω_1 and Ω_2. Ω_1 is the Euler angle between molecule 1 and the LAB z axis, and Ω_2 is the angle between the LAB z frame and molecule 2.

2.) The functional form of $P_2(w)$ decomposes into the Wigner rotation matrices when it is expressed in terms of the angles in the LAB frame. Using

$$P_2(w) \equiv D^2_{0,0}(\Omega) \tag{3}$$

$$\sum_{n=-L}^{+L} D^L_{m,n}(\Omega_1) D^L_{n,m'}(\Omega_2) = D^L_{m,m'}(\Omega) \tag{4}$$

we obtain the decomposition

$$D^2_{0,0}(\Omega) = \sum_{n=-2}^{+2} D^2_{0,n}(\Omega_1) D^2_{n,0}(\Omega_2) \tag{5}$$

To get the mean field theory, an average over all orientations of molecule 2 is taken. Then the functions of angle Ω_2 become the orientational order parameters of the system, which have to be real. By use of the relations $D^L_{m,n}(\Omega) = D^{L*}_{n,m}(-\Omega)$ and $\mathrm{Re}D^{2*}_{0,2}(-\Omega_2) = \mathrm{Re}D^{2*}_{0,-2}(-\Omega_2)$, the following result is obtained.

$$U = -a\overline{D^2_{0,0}(-\Omega_2)}D^2_{0,0}(\Omega_1) - a\mathrm{Re}\overline{D^2_{0,2}(-\Omega_2)}(D^2_{0,2}(\Omega_1) + D^2_{0,-2}(\Omega_1)) \tag{6}$$

The bar indicates thermal averages. Terms like $D^2_{0,\pm 1}$ do not obey the symmetry relations required of the molecular interaction, i.e., $D(\theta) = D(-\theta)$, so their average is zero in the distribution function. The order parameters in eq 6 are related to the macroscopic order parameters in the following way:[10]

$$Q = \overline{D^2_{0,0}}$$

$$X = \sqrt{6}\mathrm{Re}\overline{D^2_{0,2}}$$

Rewriting the $D^2_{0,n}$'s as spherical functions with $u = \cos\theta$

$$U(u,\phi) = -aQP_2(u) - \frac{aX}{2}(1-u^2)\cos 2\phi \tag{7}$$

$$Q = \overline{P_2(u)} \tag{8}$$

$$X = \frac{3}{2}\overline{(1-u^2)\cos 2\phi} \tag{9}$$

Q takes values between -0.5 and $+1.5$ and X between -1.5 and $+1.5$. The biaxial order parameter X is dependent on the uniaxial order parameter Q since it depends on $(1 - u^2) \equiv \sin^2\theta$. If the molecules are well ordered, $u \to 1$; $\theta \to 0$ or π, then $X \to 0$. Thus, making a biaxial phase more ordered (say by lowering the temperature) will reduce the biaxiality. Turning now to the partition function for the rods, we write

$$Z = \frac{1}{2\pi}\int_0^{2\pi}\int_{-1}^{1} \mathrm{d}\phi\, \mathrm{d}u \exp(-\beta U(u,\phi)) \tag{10}$$

where $\beta = 1/k_BT$. The corresponding free energy of a rod at self-consistent values of Q and X is

$$F = -k_BT\log Z - \frac{1}{2}\overline{U(u,\phi)} \tag{11}$$

where the extra term arises from the need to compensate for the double counting introduced by the mean field. At equilibrium, $\partial F/\partial Q|_X = \partial F/\partial X|_Q = 0$, which results in the self-consistency conditions

$$Q = \frac{1}{2\pi}\int_0^{2\pi}\int_{-1}^{1} \mathrm{d}\phi\, \mathrm{d}u \exp(-\beta U(u,\phi))P_2(u)/Z \tag{12}$$

$$X = \frac{1}{2\pi}\frac{3}{2}\int_0^{2\pi}\int_{-1}^{1} \mathrm{d}\phi\, \mathrm{d}u \exp(-\beta U(u,\phi))(1-u^2)\cos(2\phi)/Z \tag{13}$$

Solving numerically for the order parameters Q and X, the uniaxial Maier–Saupe results are obtained. The phase transition reduced temperature is $\tilde{T}_c = k_BT_c/a = 0.2202$, and the values of the order parameters at transition are $Q_1 = 0.4290$, $X_1 = 0$; $Q_2 = -0.2145$, $X_2 = \pm 0.6435$, showing the expected relationship $X_2 = \pm 3Q_2$.

3. The Wormlike Chain Model of a Nematic Polymer

A worm chain in a nematic field has been reduced to a spheroidal wave equation by a number of authors.[11-14] The chain is represented as a continuous curve where a point on the chain is given by $\mathbf{r}(s)$, s being the chemical length along the chain from one end. Denoting $\partial/\partial s$ by $'$ and $\mathbf{r}'(s)$ by $\mathbf{u}(s)$—the tangent vector of the curve at s—the bending energy of the chain is given in terms of the total curvature of the chain and an elastic constant ϵ. The bending energy is then $^1/_2\epsilon\int_0^L \mathrm{d}s|\mathbf{u}'(s)|^2$ where L is the total chain length. The nematic energy of a chain in a nematic mean field is $-aQ\int_0^L \mathrm{d}sP_2(u_z(s)) - {}^1/_2aX\int_0^L \mathrm{d}s(1-u_z(s)^2)\cos(2\phi(s))$ where a is now an energy per unit length and $u_z(s) = \cos(\theta(s))$ is the component of the tangent vector in the z direction. The partition function is

$$Z = \int \delta\mathbf{u}(s)\exp\left(-\frac{1}{2}\beta\epsilon\int_0^L \mathrm{d}s|\mathbf{u}'(s)|^2 + \beta aQ\int_0^L \mathrm{d}sP_2(u_z(s)) + \frac{\beta aX}{2}\int_0^L \mathrm{d}s(1-u_z(s)^2)\times \cos(2\phi(s))\right) \tag{14}$$

where $\int\delta\mathbf{u}(s)$ represents a sum over all configurations of the chain. The differential equation corresponding to the partition function is

$$\left(\frac{\partial}{\partial L} - D\nabla^2 - \beta aQP_2(u_z) - \frac{\beta aX}{2}(1-u_z^2)\cos(2\phi)\right)\Phi(\theta,\phi,L) = 0 \tag{15}$$

which represents the diffusion of the tangent vector $\mathbf{u}$ on the surface of the unit sphere with a diffusion constant $D = (2\beta\epsilon)^{-1}$, yielding an effective step length D^{-1}, characterizing the worm chain in the absence of nematic fields. Dividing through by D, measuring L in units of D^{-1}, and setting $\Phi = Sp_{n,m}\exp(-\lambda_{n,m}L)$, the wave equation becomes

$$(\lambda_{n,m} + \nabla^2 + \Delta_Q^2P_2(u_z) + \Delta_X^2(1-u_z^2)\cos(2\phi))G(\mathbf{u},\mathbf{u}_0;L,0) = \delta(\mathbf{u}-\mathbf{u}_0)\,\delta(L-0)$$

where

$$G(\mathbf{u},\mathbf{u}_0;L,0) = \sum_{n,m} Sp_{n,m}(\mathbf{u})Sp_{n,m}(\mathbf{u}_0)\exp(-\lambda_{n,m}L)$$

with $\Delta_Q^2 = \beta aQ/D$, $\Delta_X^2 = \beta aX/2D$ and where the wave functions $Sp_{n,m}(\mathbf{u})$ are normalized to 1.[15]

The propagator G can be used to evaluate the partition function and the conformations of the chain.[12]

$$Z = \int \mathrm{d}\mathbf{u}\,\mathrm{d}\mathbf{u}_0 G(\mathbf{u},\mathbf{u}_0;L,0) \tag{16}$$

If the value of L is large, then the partition function becomes dominated by the first term and the term $-k_BT \log Z$ in the free energy can be replaced by the lowest eigenvalue of the diffusion equation. This "long-chain" limit is analogous to ground-state dominance in a quantum mechanical system at long times. By use of the long-chain limit the radii of gyration of the chain are

$$\overline{r_z^2} = \sum_{n,m}\frac{2L}{\lambda_{0,0}^{n,m}}\left(\int \mathrm{d}\mathbf{u}Sp_{0,0}(\mathbf{u})\cos(\theta)\, Sp_{n,m}(\mathbf{u})\right)^2$$

$$\overline{r_x^2} = \sum_{n,m}\frac{2L}{\lambda_{0,0}^{n,m}}\left(\int \mathrm{d}\mathbf{u}Sp_{0,0}(\mathbf{u})\sin(\theta)\cos(\phi) Sp_{n,m}(\mathbf{u})\right)^2$$

$$\overline{r_y^2} = \sum_{n,m}\frac{2L}{\lambda_{0,0}^{n,m}}\left(\int \mathrm{d}\mathbf{u}Sp_{0,0}(\mathbf{u})\sin(\theta)\sin(\phi) Sp_{n,m}(\mathbf{u})\right)^2 \tag{17}$$

where the shorthand $\lambda_{0,0}^{n,m} = \lambda_{n,m} - \lambda_{0,0}$ has been used. The propagator can be solved using perturbation theory or numerically using a matrix diagonalization in the basis of the spherical harmonics. The radii of gyration calculated using a pertubation expansion of the propagator, expressed in terms of the coupling constants Δ_Q^2 and Δ_X^2, are as follows, after dividing through by the isotropic radius of gyration for a wormlike chain.[12]

$$\overline{r_x^2} = 1 - \frac{\Delta_Q^2}{6} + \frac{\Delta_X^2}{3} - \frac{4\Delta_Q^2\Delta_X^2}{45}$$

$$\overline{r_y^2} = 1 - \frac{\Delta_Q^2}{6} - \frac{\Delta_X^2}{3} + \frac{4\Delta_Q^2\Delta_X^2}{45}$$

$$\overline{r_z^2} = 1 + \frac{\Delta_Q^2}{3} + \frac{(\Delta_Q^2)^2}{15} - \frac{4(\Delta_X^2)^2}{135} \tag{18}$$

For example, if the chain is in a biaxial state with a large Q and a small finite X, eqs 18 show that the chain backbone adopts a transversely flattened prolate ellipsoidal shape with the long axis in the z direction. The average value of the radius of gyration for the whole molecule is quadratic in both order parameters. Therefore positive or negative order parameters increase the molecular volume to a first approximation.

4. A Mean Field Theory of Combs

In this mean field theory of combs each component of the system, i.e., the backbone chains and the side-chain rods, contributes toward a self-consistent field via which the constituent molecules interact. Since there are two fields associated with each component there are in total four fields, and also four order parameters Q and X for the main and side chains. Consider placing a rod in the fields. It will feel an interaction from its own two rod fields, and from the two backbone fields. It is necessary to parameterize these interactions in a way consistent with the composition and dimensions of the constituent molecules. This is done by following the procedure used in ref 2.

At least five influences on molecular order can be envisaged. The corresponding energies are as follows: (i) v_a, the drive toward parallel order of the side chains; (ii) v_b, the drive toward parallel order of the main chains caused by having stiff, mesogenic units included in the main chain; (iii) v_c, the same nematic coupling between the main and side chains making for parallel order between the two; (iv) v_f, the stiffness of the "hinge" joining the side and main chains together; (v) ϵ, the bending energy coefficient of the main chain.

The volume fraction of the two components will also weight their interaction. The balance between main and side chains could be altered by either altering the number of side chains attached to the main chain per unit length or altering the length of the side chains.

Assuming that there is a common cross-sectional dimension ℓ of the side and main chains, that the length of the side chain divided by this dimension is x, and that the length of main chain per side chain in these units is n, then the volume fraction of side chain is

$$\chi = x/(n + x) \tag{19}$$

In the results presented, ψ is varied at fixed x, by changing n. The fraction of segments that are side chains seen by a segment of length ℓ is χ, and the fraction of segments that are main chains seen by a segment is $1 - \chi$. There is always, of course one hinge per side chain.

The mean field potential of one side chain is then

$$U_a = -(\chi v_a xQ_a + \{(1-\chi)v_c x - v_f\}Q_b)P_2(u) - (\chi v_a xXa + \{(1-\chi)v_c x - v_f\}X_b)\frac{(1-u^2)}{2}\cos(2\phi) \tag{20}$$

and the potential of the main chain is

$$U_b = -((1-\chi)v_bQ_b + (\chi v_c - v_f/n)Q_a)\frac{1}{\ell}\times \int_0^L \mathrm{d}sP_2(u_z(s)) - ((1-\chi)v_bX_b + (\chi v_c - v_f/n)X_a)\frac{1}{2\ell}\times \int_0^L \mathrm{d}s(1-u_z(s)^2)\cos(2\phi(s)) \tag{21}$$

Q_a, X_a are the side chain, and Q_b, X_b are the main chain order parameters. In the cross-coupling the hinge effect v_f enters with opposite sign to the nematic effect v_c since we assume that it is such that the side chain in naturally perpendicular to the main chain. The competition between ordering parallel or perpendicular to the main chain can immediately be seen in the combination of v_c and v_f in the potentials. What is important is the overall sign of the combination denoted by $\bar{v}_c = v_c - v_f/n\chi$, obtained by dividing the cross-coupling terms in eqs 20 and 21 by $1 - \chi$ and χ, respectively. Thus, the structure of the theory is really determined by the *three* interactions $(1 - \chi)v_b$, χv_a, and $\bar{v}_c$ and not the full five mentioned above. We reiterate that the component parts of the polymer are taken to by cylindrical so that there are only a single v_a and a single v_b. It is possible to construct side-chain PLCs with different $\bar{v}_c$'s by altering the chemical composition of a spacer unit joining a side-chain nematogen to the main chain.[16]

In order to proceed numerically it helps to make the interaction variables dimensionless and choose a suitable reduced temperature. v_b is chosen and extracted from the expressions for U_a and U_b. The other interaction variables divided by v_b are denoted by a $'$. To solve the diffusion equation expressions for the two coupling constants Δ_Q^2 and Δ_X^2 are needed which are obtained from U_b. These expressions, together with the reduced variable version of eq 20 are

$$\Delta_Q^2 = \frac{2}{\tilde{T}^2}[(1-\chi)Q_b + \chi\bar{v}'_c Qa] \tag{22}$$

$$\Delta_X^2 = \frac{1}{\tilde{T}^2}[(1-\chi)X_b + \chi\bar{v}'_c Xa] \tag{23}$$

$$\beta U_a = -\frac{x\sqrt{v_b/\epsilon\ell^{-1}}}{\tilde{T}}[\chi v'_a Qa + (1-\chi)\bar{v}'_c Qb]P_2(u) - \frac{x\sqrt{v_b/\epsilon\ell^{-1}}}{2\tilde{T}}[\chi v'_a Xa + (1-\chi)\bar{v}'_c X_b] \times (1-u^2)\cos(2\phi) \tag{24}$$

Chain lengths have again been reduced by D^{-1} and the reduced temperature is

$$\tilde{T}^2 = (kT)^2/(\epsilon v_b/\ell) \tag{25}$$

The reduction in temperature follows ref 2, which corresponds to the N_{II} phase at $\chi = 0$. The limit of $\chi = 0$ can be achieved by letting $x \rightarrow 0$ or $n \rightarrow 0$. However, in this model the $x \rightarrow 0$ limit is inaccessible because the hinge always affects the backbone regardless of the length of the side chain (see eqs 22 and 23).

Free energies of one side chain and a whole main chain are

$$F_a = -kT\log Z_a - \frac{1}{2}\bar{U}_a \equiv xf_a \tag{26}$$

$$F_b = -kT\log Z_b - \frac{1}{2}\bar{U}_b \equiv Nf_b \tag{27}$$

The free energy of a repeat unit is then $xf_a + f_b n\ell/D^{-1}$, which converts to a free energy per unit volume f of

$$f = \chi f_a + \frac{(1-\chi)}{\alpha}f_b \tag{28}$$

where $\alpha = D^{-1}/\ell$ is the number of segments in a persistence length. The free energy of the isotropic phase is $f_I = -\chi \ln(2)/x - (1-\chi)\ln(2)/\alpha$, which is subtracted off all subsequent free energies.

The self-consistency conditions for the order parameters of the comb free energy (eq 28) are obtained by differentiating the free energy partially with respect to the order parameters. In fact the backbone and side-chain parts of the free energy depend only on fixed combinations of the Q's and X's. Writing the partition functions $Z_a[p_1, q_1]$ and $Z_b[p_2, q_2]$ instead as functions of p_1, q_1, p_2, and q_2 where

$$p_1 = (\alpha_1 Q_a + \gamma_1 Q_b) = \frac{x\sqrt{v_b/\epsilon\ell^{-1}}}{\tilde{T}}(\chi v'_a Qa + (1-\chi)\bar{v}'_c Q_b)$$

$$q_1 = (\alpha_1 X_a + \gamma_1 X_b) = \frac{x\sqrt{v_b/\epsilon\ell^{-1}}}{\tilde{T}}(\chi v'_a X_a + (1-\chi)\bar{v}'_c X_b)$$

$$p_2 = 2(\alpha_2 Q_b + \gamma_2 Q_a) = \frac{2}{\tilde{T}_2}((1-\chi)Q_b + \chi\bar{v}'_c Q_a)$$

$$q_2 = (\alpha_2 X_b + \gamma_2 X_a) = \frac{1}{\tilde{T}_2}((1-\chi)X_b + \chi\bar{v}'_c X_a) \tag{29}$$

then helps make the symmetry of the problem more apparent. The constants α_1, α_2, γ_1, and γ_2 now contain all the relevant $\tilde{T}$ information, etc. If we now define four new functions $g_{ap_1}[p_1, q_1]$, $g_{aq_1}[p_1, q_1]$, $g_{bp_2}[p_2, q_2]$, and $g_{bq_2}[p_2, q_2]$ where, for instance, $g_{ap_1}[p_1, q_1] = (\partial/\partial_{p_1})\log Z_a[p_1, q_1]$ and the other functions are similarly defined, then the self-consistency conditions are

$$Q_a = g_{ap_1}[(\alpha_1 Q_a + \gamma_1 Q_b), (\alpha_1 X_a + \gamma_1 X_b)]$$

$$X_a = g_{aq_1}[(\alpha_1 Q_a + \gamma_1 Q_b), (\alpha_1 X_a + \gamma_1 X_b)]$$

$$Q_b = g_{bq_2}[2(\alpha_2 Q_b + \gamma_2 Q_a), (\alpha_2 X_b + \gamma_2 X_a)]$$

$$X_b = g_{bq_2}[2(\alpha_2 Q_b + \gamma_2 Q_a), (\alpha_2 X_b + \gamma_2 X_a)] \tag{30}$$

The self-consistency conditions of the comb show explicitly the structure of the theory. Each component can be thought of as an independent nematic element in an external field. The external field is the mean field of the other nematogen moderated by the strength of the cross-coupling between the two components. When the cross-coupling equals 0 (the vanishing of the γ terms in eq 30), the two components, the main and side chains, are independent, and the order parameters depend only on the strength of the "self"-interaction (the α terms) and the "self" order parameters.

5. Results

5.1. General Discussion. The architecture of the comb molecule determines the phase behavior of the system. Values of the molecular coupling constants are chosen to illustrate the qualitative behavior of such molecules, rather than to try to model any particular molecule. Accordingly, values of v_a, v_b, v_c, v_f, and ϵ/ℓ are chosen along with values for x and χ to determine a particular molecular shape. The minimum of the free energy (eq 28) at self-consistent values of Q_a, X_a, Q_b, and X_b determines the equilibrium behavior of the system, the system adopting the conformation of the lowest free energy. The minimum of the free energy can be determined numerically either by explicitly solving for the four self-consistency conditions of the order parameters or by a minimization of the free energy in the four-dimensional space of the order parameters; both are of course equivalent.

Figure 3 shows the phase diagram for a system which, by varying χ at a fixed value of x, displays all the principal ordered phases N_I, N_{II}, N_{III}, N_{IB}, and N_{IIB} as well as I, and isotropic phase. The solid lines denoted first-order phase transitions; the dashed lines denoted second-order phase transitions.

The principal sequence of transitions traversing the phase diagram horizontally can be understood by looking at the variation of $\bar{v}'_c$, which determines the relative sign of the order parameters Q_a and Q_b and of X_a and X_b, as can be seen in eqs 22–24. With the choice of coupling constants in Figure 3, $\bar{v}'_c$ changes sign at $\chi = 0.375$. To the right of this point $\bar{v}'_c$ is negative, forcing the side chains to be ordered perpendicular to the main chain—resulting in the phases N_I, N_{II}, etc., but to the left of this point $\bar{v}'_c$ is positive, and the main and side chains want to align, resulting in the N_{III} phase.

We now look at the effect of lowering the temperature of a given comb system. To the right of the phase diagram the effect of the side chains is dominant as the strength of side-chain interations is governed by their volume fraction χ. At high temperatures the melt is isotropic,

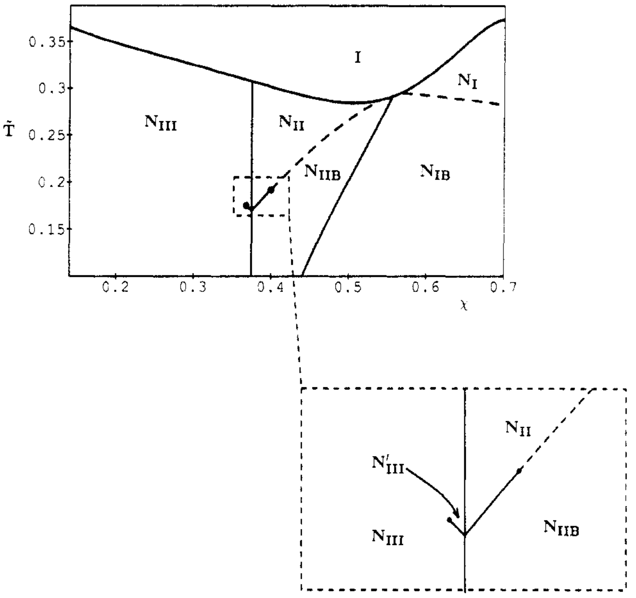

Figure 3. Phase diagram of comb polymers with coupling constants in the ratio $v_a:v_b:v_c:v_f:\epsilon/\ell$ = 1:2:1.2:3:2 with the axial ratio of the side chains being $x = 4$. Reduced temperature $\tilde{T}$ is plotted versus side-chain volume fraction χ. The phase diagram is dominated by side chains in the N_I, N_{IB} region of high χ, otherwise by the main chains. The sign of the main-chain–side-chain coupling $\tilde{v}'_c$ changes at $\chi = 0.375$, separating the N_{III} from the N_{II} phases. The line separating the N_{IB} from the N_{IIB} phases is arbitrary; see section 5 for the criterion used. The phase lines separating the N_I and N_{II} phases from their biaxial counterparts are dashed (second order) or solid (first order) transitions. The tricritical point (χ_c, $\tilde{T}_c$) is at (0.4, 0.2).

but on cooling, the side chains order and force the backbone into the xy plane, forming the N_I phase. If the phase is then further cooled, the backbones take the opportunity to order in the xy plane, lowering their energy. This phase where the backbones become ordered after the side chains is denoted as N_{IB}—see Figure 4 where $\chi = 0.65$. When the phase becomes biaxial at $\tilde{T} \simeq 0.29$, the backbones order in the xy plane, with order parameters $Q_b < 0$, $X_b > 0$. This is essentially a uniaxial phase aligned with its principal axis in the x direction, but viewed from the z direction. The real biaxiality as shown by the dotted line in Figure 4 is extracted from the order parameter matrix as described in section 2. The side-chain component has $Q_a > 0$, $X_a < 0$, and therefore, X_a represents the real biaxiality of the side chains. Upon further cooling the amount of biaxiality decreases, as increasing uniaxial order destroys the biaxiality. The biaxiality of each component arises from the geometry of attachment of the side and main chains and can be understood by use of the following argument. First consider a system of nematic rods aligned with the director along the z axis. If $T \neq 0$ the rods will be imperfectly aligned, and deviations away from the z axis cost energy. This energy cost is aximuthally symmetric about z. Now consider a comb phase, such as the N_{IB} phase mentioned above. Take, for instance, the side chains which are aligned along z. Deviations by the nematogens away from the z direction still cost energy, but the energy cost is not aximuthally symmetric about z, as the field of the main chains aligned in the x direction increases the energy of deviations in this direction. Therefore the deviations away from the z axis will be on average in the y direction, and the side chains will be biaxial. The reduction in the biaxiality at lower temperature is as expected; see the comments after eq 9, where the nature of the biaxial phase is discussed.

Moving toward the left of the phase diagram, the effect of the side chains becomes weaker. Cooling from the isotropic phase at values of χ less than $\simeq 0.55$ results first in an N_{II} phase, where the backbone is ordered, and the side chains are forced into the xy plane. Further cooling results in a phase transition to an N_{IIB} phase, caused by subsequent ordering of the side chains; see Figure 5 for the case of $\chi = 0.46$.

In fact the amount of biaxiality in each component of the comb molecule is governed by the strength of the intermolecular coupling. The stronger the coupling, the stronger the biaxiality of each component. Therefore on the high χ side of the phase diagram the biaxiality should be greater. In Figures 4–6 this can clearly be seen, with the weakest biaxiality seen when $\chi = 0.38$ (Figure 6), where $\tilde{v}'_c$ is almost zero, and the strongest when $\chi = 0.65$ (Figure 4) when $\tilde{v}'_c$ is much larger.

The distinction between the two phases N_{IB} and N_{IIB} is purely arbitrary, since at any given point in the phase diagram there are at least three different sets of order parameters that results in the same free energy, which correspond to describing the phase aligned parallel to the x, y, or z direction. For the phases which only have one positively ordered component, N_I and N_{II}, it is obvious which description should be chosen—the one which results in an ordered phase parallel to the z direction giving a positive uniaxial order parameter. For the biaxial phases it is less clear how the system should be described, since the system has one component almost uniaxially ordered, for instance, parallel to the z direction, with another component ordered almost uniaxially along the x or y direction. The chosen distinction made between the two phases is based upon which component has the largest value of its uniaxial order parameter measured in its own z coordinate system, i.e., in its own principal frame. If the largest value of uniaxial order parameter is given by the side-chain (main-chain) component, the phase is called N_{IB} (N_{IIB}). This arbitrary distinction results in the line separating the N_{IB} and N_{IIB} phases.

There are similarities between the second ordering transition (the side chains in Figures 5 and 6 and the main chains in Figure 4) and that of a system of nematic rods ordering in an external field. The problem of nematics ordering in external fields has been extensively discussed for the case where the field increases the order of the nematic phase.[17,18] In the comb system, for instance, in the N_{IIB} case, the field is provided by the backbone pushing the side-chain rods into the xy plane, at first inducing a negative Q_a followed by an ordering transition at a lower temperature to a state with side chains primarily aligned in the xy plane. The effect of the main chains on the side chains can be modeled by that of a "negative electric field" which forces the rods into the xy plane. The interaction of conventional nematic rods has to be modified to include this field, V, resulting in a partition function

$$Z = \frac{1}{2\pi}\int_0^{2\pi}\int_{-1}^{1} \mathrm{d}\phi\, \mathrm{d}u\, \exp\left\{\frac{(Q - V^*)}{T^*}P_2(u) + \frac{X}{2T^*}(1 - u^2)\cos(2\phi)\right\} \quad (31)$$

where $u = \cos\theta$, $T^* = k_BT/a$, and V has also been reduced by a, i.e., $V^* = V/a$. Substituting this partition function into the previously obtained free energy (eq 11) for the rod system allows the equilibrium values of the two order parameters to be determined at constant T^* and V^*. The self-consistency conditions can be written in a manner similar to eq 30. Defining $p = (Q - V^*)/T^*$ and $q = X/2T^*$, and the functions $g_p[p, q]$ and $g_q[p, q]$ in a manner similar to before, i.e., $g_p[p, q] = (\partial/\partial_p) \log Z[p, q]$, the

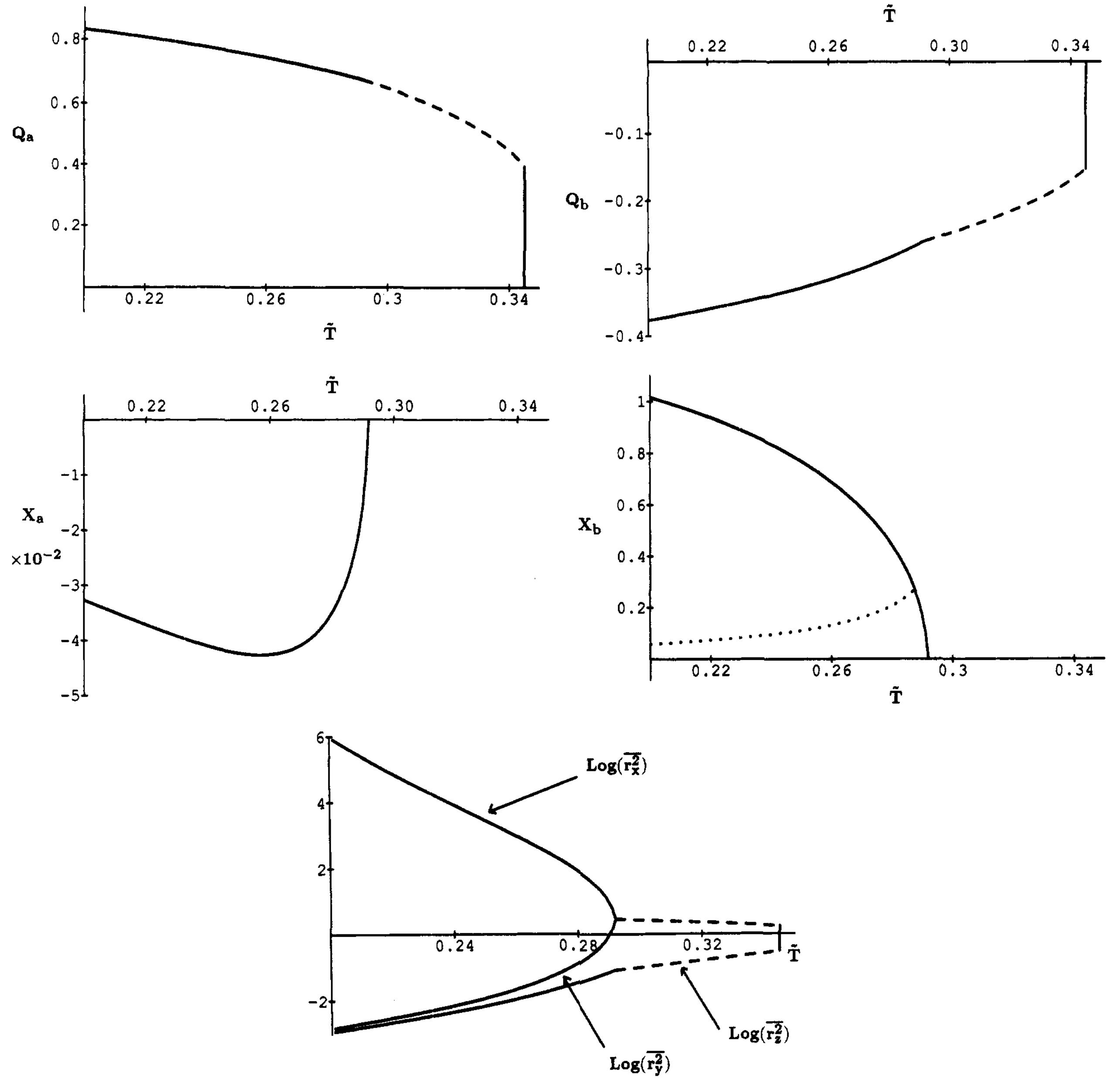

Figure 4. Comb phase order parameters for side-chain volume fraction $\chi = 0.65$. Uniaxial (Q) and biaxial (X) order parameters are shown for the backbone (b) and side-chain (a) components. The side chains order first, forming a uniaxial phase (dashed lines) at $\tilde{T} \simeq 0.345$ with $Q_a > 0$, $Q_b < 0$—the backbones are directed toward the perpendicular plane. The chain conformation is an oblate spheroid, i.e., $\overline{r_z^2} < 1$, $\overline{r_x^2} = \overline{r_y^2} > 1$. At $\tilde{T} \simeq 0.29$ the backbones order in the perpendicular plane via a second-order transition forming a biaxial phase (smooth lines). The dotted line shows the reali biaxiality of the backbone, as discussed in section 2. X_a represents the real biaxiality in the side chains. $\overline{r_x^2}$ and $\overline{r_y^2}$ split as the chain adopts a flattened prolate ellipsoidal shape with the long axis in the x direction.

self-consistency conditions are

$$Q = q_p[(Q - V^*)/T^*, X/2T^*]$$

$$X = g_q[(Q - V^*)/T^*, X/2T^*] \tag{32}$$

In the limit where $V^* \to \infty$, the free energy can be investigated asymptotically and the coefficients of a Landau theory obtained, which predicts a second-order phase transition. When $V^* = 0$, the conventional Maier–Saupe result holds and there is a phase transition which is first order to the nematic state. So, there must be some critical value of V^* where the crossover from first- to second-order phase transitions occurs. This is investigated numerically, and the resulting critical value is $V_c^* \simeq 1.46$.

If the comb molecule self-consistency equations are similar in some limit to the negative field equations, we can use the negative field model to explain the comb behavior in this limit. Examining the $\mathrm{N_{II}}$ phase where $\bar{\nu}'_c \to 0^-$, the $\mathrm{N_{II}}$ phase is very well established as the temperature where the transition to $\mathrm{N_{IIB}}$ takes place. Q_b is therefore larger and has a rather low temperature dependence and $X_b = 0$. The side-chain self-consistency conditions in this limit are, from eq 30

$$Q_a \simeq g_{ap_1}[(\alpha_1 Q_a + \gamma_1 Q_b), (\alpha_1 X_a)]$$

$$X_a \simeq g_{aq_1}[(\alpha_1 Q_a + \gamma_1 Q_b), (\alpha_1 X_a)] \tag{33}$$

where γ_1 is negative. The correspondence between eqs 32 and 33 is clear, and we should expect the $\mathrm{N_{II}} \to \mathrm{N_{IIB}}$ phase transition line to show a tricritical point. The phase transition between the $\mathrm{N_{II}}$ and $\mathrm{N_{IIB}}$ phases is first order, as predicted when $\chi = 0.38$ (see Figure 6). Moving further

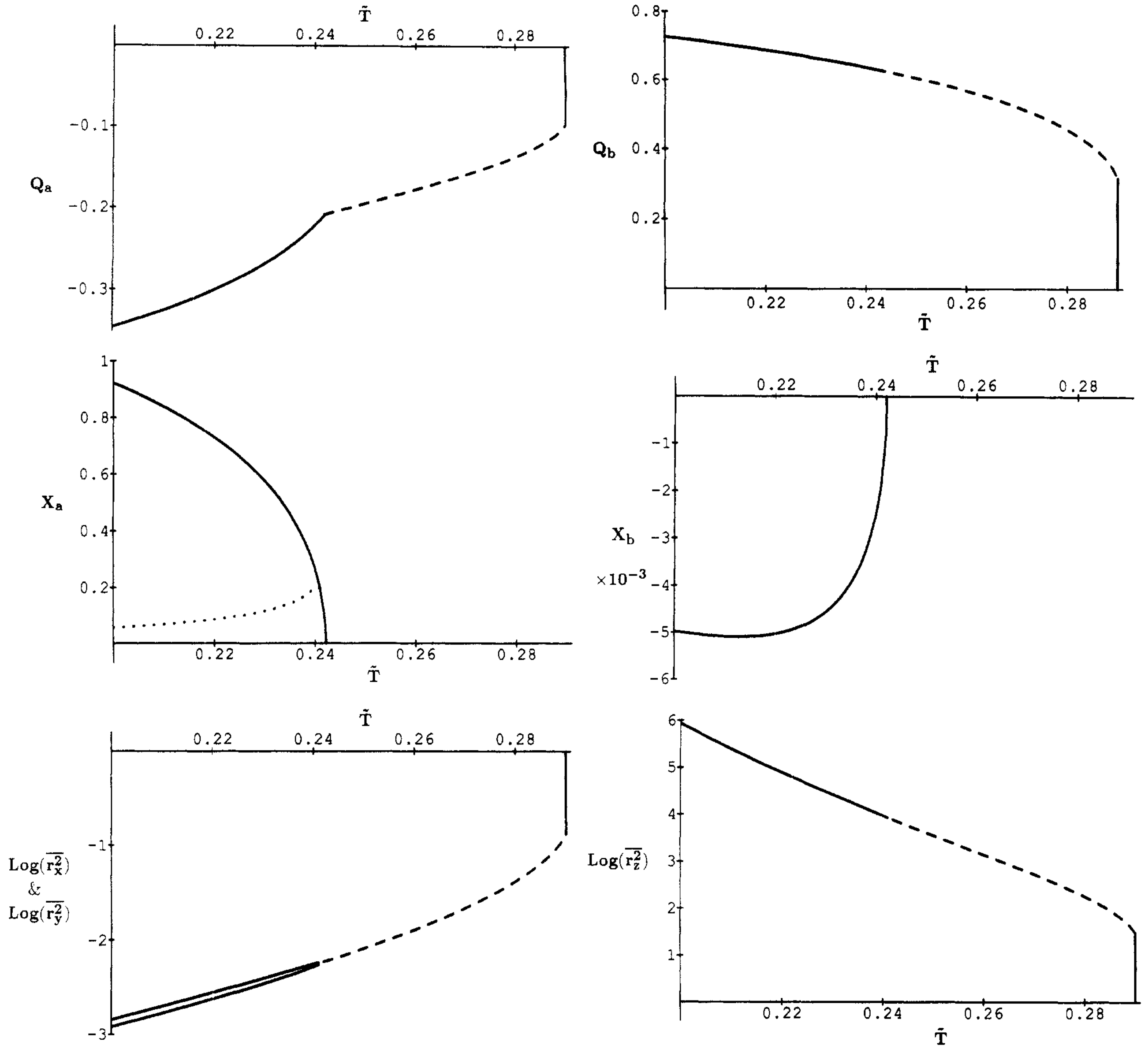

Figure 5. Comb phase order parameters Q_a, Q_b, X_a, and X_b for side-chain volume fraction $\chi = 0.46$. The main chain now orders first, $Q_b > 0$, and defines the principal axis of the phase N_{IIB}. The chain conformation in the N_{II} phase is a prolate ellipsoid with the long axis pointing in the z direction. At lower temperatures the side chains order in the perpendicular plane toward which they have been forced. The transition is second order. The chain conformation becomes a flattened prolate ellipsoid in the biaxial phase, with the biaxiality disappearing as $\tilde{T} \to 0$. Other aspects of the figure are as in Figure 4.

across the phase diagram the value of $\bar{v}'_c$ increases, increasing the value of the effective field that the side chains see from the main chains. At some point this value of the effective field becomes sufficiently large that the phase transition becomes second order. At $\chi = 0.46$ the phase transition has indeed become second order (see Figure 5). There must therefore be a tricritical point in between these two χ values where the phase transitions become second order. This point is denoted by χ_c. The transition between N_I and N_{IB} is always second order, suggesting that if the negative field model applies, then $\bar{v}'_c$ is too large for the transition ever to be first order.

5.2. The N_{III} Phases. To the left of the line $\chi = 0.375$ in Figure 3, $\bar{v}'_c > 0$, and only the N_{III} phases are stable. Again there are similarities between the ordering of the side chains in the field of the backbone and the ordering of a conventional nematic in an external field, but one which increases rod order in the direction of the field, such as an electric or magnetic field. Accordingly there is a first-order transition between the paranematic phase, denoted by N'_{III}, where the ordering of the side chains is small and caused by the external field, to a nematic phase N_{III} which takes place at a higher temperature than the zero-field transition temperature (i.e., the temperature at $\bar{v}'_c = 0$). This line of phase transitions terminates at a critical point, which is discussed further in ref 19.

5.3. Radii of Gyration. Changes in the ordering of the comb have dramatic consequences for the backbone chain conformation. In the N_{II} phase, the chain conformation is prolate spheroidal, with cylindrical symmetry in the xy plane and with the long axis aligned parallel to the z direction. Upon cooling to the N_{IIB} phase, the symmetry in the xy plane is lost and the chain adopts a conformation that is anisotropic in three directions. The shape is spheroidal, but squashed in the x direction. This slight splitting of the xy symmetry is due to the small amount of biaxiality present in the backbone order parameter. The shape phase transition is second order in Figure 5 and first order in Figure 6, agreeing with the phase transitions of the order parameters themselves.

The N_I to N_{IB} conformation changes are more dramatic. In the N_I phase the backbone is forced into the xy plane by the side chains, and the backbone conformation becomes an oblate spheroid. Then, cooling to an N_{IB} phase,

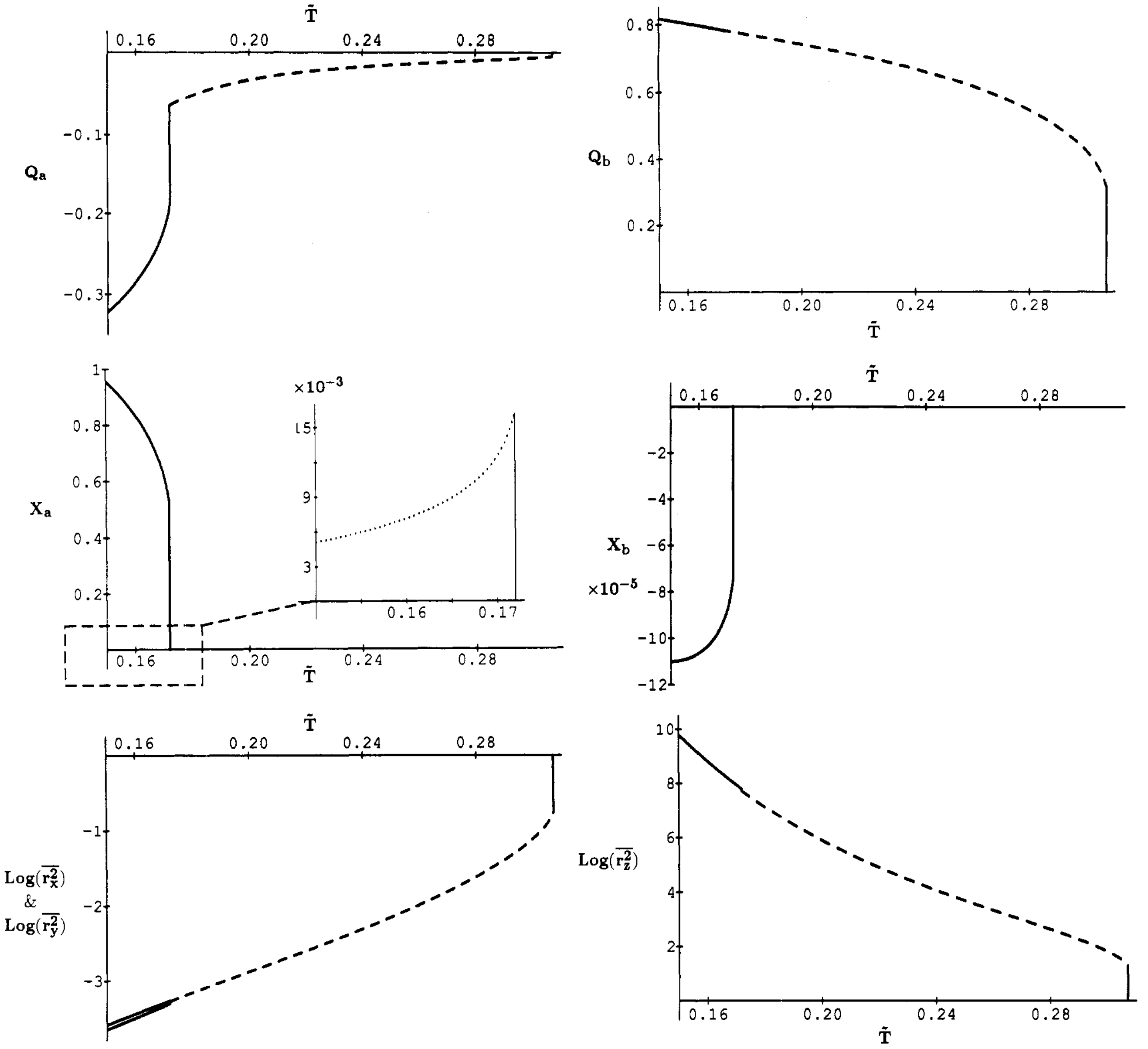

Figure 6. Comb phases for volume fraction of side chain $\chi = 0.38$. This is close to the volume fraction where the effective cross coupling $v'_c \to 0$. The uniaxial–biaxial transition is now first order as expected.

the xy symmetry breaks and the molecule adopts a prolate spheroidal shape identical to that of the N_{IIB} phase, but aligned in the x direction. In both the N_{IB} and N_{IIB} phases the anisotropy in the third direction decreases as the temperature decreases, as the biaxiality in the backbone order parameter decreases with temperature. This is easily visible in Figure 4 where $\overline{r_z^2}$ approaches $\overline{r_y^2}$ as the temperature decreases.

6. Conclusions

Comb polymers, even when they are comprised of uniaxially symmetric components, are shown to be able to form biaxial phases. This is because of the geometry of attachment of the side chains to main chains. Biaxial phases are shown to be the intermediates in going between the N_I and N_{II} uniaxial phases. The principal axis of each of these uniaxial phases rotates by 90° as one makes this shift in phase type. The difference between the newly predicted biaxial phases N_{IB} and N_{IIB} is simply a matter of degree—it is the point where one should sensibly consider the principal axis of the whole to have made a 90° shift. Both first and second order uniaxial to biaxial transitions are found, depending on the strength of the cross coupling between main and side chains. We hope that one can apply these qualitative predictions of new nematic phases to classifying the complex comb and combined phases that have been synthesized. In addition we have applied these ideas to biaxial distortions of nematic rubbers and also of classical networks with residual nematic interactions.

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References and Notes

(1) Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Makromol. Chem.* **1985**, *186*, 1951.
(2) Wang, X. J.; Warner, M. *J. Phys. A.: Math. Gen.* **1987**, *20*, 713.
(3) Rusakov, V. V.; Shliomis, M. I. *Vysokomol. Soedin. Ser. A* **1987**, *29*, 1195; *Polym. Sci. USSR (Engl. Transl.)* **1987**, *29*, 1323.
(4) Frieser, M. J. *Phys. Rev. Lett.* **1973**, *24*, 1041.
(5) Yu, L. J.; Saupe, A. *Phys. Rev. Lett.* **1980**, *45*, 1000.
(6) Chandrasekhar, S.; Sadashiva, B. K.; Ratna, B. R.; Raja, V. N. *Pramāna* **1988**, *30*, L491.

(7) Renz, W. Proceedings of the International Conference on Liquid Crystal Polymers, Bordeaux, July 20–24, 1987. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 549.

(8) Gramsbergen, E. G.; et al. *Phys. Rep.* **1986**, *135* (4), 195.

(9) Maier, E.; Saupe, A. *Z. Naturforsch.* **1959**, *14A*, 882.

(10) Zannoni, C. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979.

(11) Jähnig, F. *J. Chem. Phys.* **1979**, *70*, 3279.

(12) Warner, M.; Gunn, J. M. F.; Baumgärtner, A. *J. Phys. A: Math. Gen.* **1985**, *18*, 3007.

(13) ten Bosch, A.; Maissa, P.; Sixou, P. *Phys. Lett.* **1983**, *94A*, 299; *J. Chem. Phys.* **1983**, *79*, 3462.

(14) Rusakov, V. V.; Shliomis, M. I. *J. Phys. Lett.* **1986**, *46*, L-935.

(15) The $Sp_{n,m}(\mathbf{u})$ are not the usual spheroidal wave functions as defined in: Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics, Part 2*; McGraw-Hill: New York, 1953; p 1576. Our $Sp_{n,m}(\mathbf{u})$ wave functions are normalized to 1, and the defining potential is not simply u_z^2.

(16) Mitchell, G. R.; Coulter, M.; Davis, F. J.; Guo, W. *J. Phys. 2* **1992**, *2*, 1121.

(17) Hornreich, R. M. *Phys. Lett.* **1985**, *109A*, 232.

(18) Wojtowicz, P. J.; Sheng, P. *Phys. Lett.* **1974**, *48A*, 235.

(19) Renz, W.; Warner, M. *Proc. R. Soc. London* **1988**, *A417*, 213.